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The Measurement of Some Standard Wave-Lengths in the Infra-Red Spectra of the Elements

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THE MEASUREMENT OF SOME STANDARD WAVE-LENGTHS IN THE INFRA-RED SPECTRA OF THE ELEMENTS.

By EXUM PERCIVAL LEWIS.

THE investigation described in the following pages was begun nearly two years ago, with the object of extending Professor Rowland's table of standard wave-lengths beyond the region which can be studied by optical and photographic means. Owing to the difficulty of devising apparatus sufficiently sensitive to measure the small differences of temperature involved, and to the fact that continuous work on the experiment has been impossible, only a few wave-lengths have so far been determined. Although their measurement has not been so exact as in the case of visible lines, the result is a much closer approximation to the truth than has hitherto been obtained.

HISTORICAL REVIEW.

Before describing the experimental methods and discussing the results, a brief sketch of the most important work which has been done previously in this field will be given.

It appears that the first evidence of the existence of radiation beyond the red of the visible solar spectrum was discovered by

Sir William Herschel,[1] who, in 1800, observed a rise of the mercury in thermometers placed in that region. He also demonstrated that this radiation obeys the same physical laws as light itself.

In 1840 Sir John Herschel[2] studied this region of the solar spectrum by exposing in it a strip of paper covered on the back with lampblack and moistened with alcohol. While moist the paper was transparent, and revealed the dark background, which would gradually disappear as the liquid evaporated. He noticed that the alcohol dried more rapidly in some places than in others, and inferred from this the existence of several absorption bands in the infra-red of the solar spectrum. Unfortunately, Herschel did not use a slit, but threw the image of the Sun directly upon his prism. Under these conditions it has been doubted whether absorption bands could be detected. Lord Rayleigh and J. W. Draper repeated the experiment, and failed to secure definite results.[3]

J. W. Draper[4] discovered in 1842 the existence of three absorption bands, and indications of a fourth, in the infra-red of a photograph of the solar spectrum taken by him on a plate of iodide of silver.

In 1846[5] Fizeau and Foucault rediscovered these bands by means of mercurial thermometers with bulbs of small diameter; and they were again observed in 1871 by Lamanski,[6] who by means of a thermopile drew an intensity curve for the entire solar spectrum up to a wave-length of about 9400 Ångström units. Mouton[7] and Desains[8] subsequently investigated the distribution of energy in the solar spectrum in the same manner.

A very different method was adopted by E. Becquerel[9] for the

[1] *Phil. Trans.* 1800.
[2] *Phil. Trans.* 1840.
[3] *Phil. Mag.* **4**, 348, 1877; *Phil. Mag.* **11**, 159, 1881.
[4] *Phil. Mag.* **24**, 456, 1842.
[5] *C. R.* **25**, 449, 1847.
[6] *Pogg. Ann.* **146**, 207, 1872.
[7] *C. R.* **87**, 298, 1879.
[8] *C. R.* **95**, 435, 1882.
[9] *C. R.* **69**, 999, 1869; **77**, 302, 1873; **83**, 249, 1876.

study of this region. He threw the spectrum formed by a carbon bisulphide prism upon a screen covered with phosphorescent material, and on the infra-red region superimposed the violet and ultra-violet spectrum formed by another prism. The phosphorescence excited by the superimposed rays would be extinguished by the infra-red radiation, while those portions of the screen on which absorption bands fell would remain faintly luminous. By the application of Cauchy's dispersion formula he then calculated the wave-lengths of these bands.

Henri Becquerel[1] repeated the experiments of his father by throwing the infra-red spectrum upon phosphorescent plates which had been exposed previously to sunlight. He noted two distinct phases in the resulting phenomena. First, especially if the previous exposure had been brief, the phosphorescence of those portions of the plate on which the radiation fell would be stimulated to greater activity, showing by contrast the spaces covered by absorption bands as dark lines, as in a positive photographic plate. After a short time the luminous energy of the over-excited parts of the plate would be exhausted, and the spectral bands would then appear bright on a dark background, as in a photographic negative. He used glass plates covered with various phosphorescent materials, such as the sulphides of calcium, barium, and strontium, and noted the important fact that there were certain regions of the spectrum characteristic of each substance in which no effect on the phosphorescence could be observed. These regions might easily be mistaken for absorption bands, and show the necessity for great caution in using this method. Becquerel examined the spectra formed by a diffraction grating in this way. From the overlapping spectrum of the second order he determined the approximate wave-lengths of bands in the solar spectrum up to about 14,000 Ångström units. He also used a prism calibrated in the infra-red by the solar bands measured as above, and from the phosphorographs of the spark and arc-spectra of various metals determined the approximate wave-lengths of some of the more prominent lines, which he

[1] *C. R.* **96**, 121, 1883.

regarded as accurate to one or two millionths of a millimeter (ten or twenty Ångström units).[1] He also observed many diffuse bands which he believed to be groups of lines.

In 1880 Abney[2] succeeded in photographing the solar spectrum to a wave-length of about 10,000 Ångström units on bromide of silver plates prepared by a special process. A few years later he photographed the spectrum formed by a Rowland concave grating, and published an extended table of infra-red wave-lengths which he regarded as accurate to about one-tenth of an Ångström unit.[3] He attempted by the same process to photograph the infra-red arc-spectra of various metals.[4] In the case of sodium he succeeded in detecting the existence of a pair of lines of wave-lengths about 8187 and 8199. He does not give the probable error of these figures. In the spectrum of calcium he discovered evidences of lines having wave-lengths between 8500 and 8600. For all the other metals tried he obtained negative results.

E. Pringsheim[5] studied the distribution of energy in the solar spectrum for some distance in the infra-red by means of a Crookes radiometer. This instrument consisted of a narrow vane supported by a bifilar suspension. The deflections produced by radiation falling on the vane were indicated by a beam of light reflected from a mirror attached to it.

A most elaborate investigation of the infra-red of the solar spectrum has been carried on for many years by Professor Langley.[6] After attempting without success to obtain sufficient sensitiveness from a thermopile, in 1879 he devised the bolometer, which indicates temperature differences by the variation of the resistance of a small strip of platinum forming one arm of a Wheatstone bridge. He has gradually improved this instrument and the galvanometer which indicates variations of the current

[1] *C. R.* **96**, 1217, 1883; **97**, 71, 1883; **99**, 374, 1884.
[2] *Phil. Trans.* 1880, p. 653.
[3] *Ibid.* 1886, p. 457.
[4] *Proc. R. S.* **32**, 443, 1881.
[5] *Wied Ann.* **18**, 32, 1883; *Phil. Mag.* **43**, 282, 1872.
[6] *Proc. Am. Acad.* **16**, 1881.

until, as he now states, it will indicate temperature differences almost as small as a millionth of a degree. He has investigated the distribution of energy in the solar spectrum up to a wave-length of nearly 60,000 Ångström units, or over a region about thirteen times as long as the visible spectrum, when expressed on the normal scale. To determine the wave-lengths of absorption bands he has used both the diffraction grating and glass and rock-salt prisms calibrated by comparison with a grating. Recently he has greatly improved the method of observation by substituting for the former tedious method of eye observation an ingenious automatic process of making the bolographs.[1] By another automatic device he translates the curves thus obtained into line spectra resembling the photographs of the visible spectrum.

A full account of Langley's recent work is given in the report for 1894 of the British Association. A note in THE ASTROPHYSICAL JOURNAL for February, 1895, briefly describes his method, and gives illustrations comparing the results obtained by Sir John Herschel, Lamanski, and Langley.

Draper[2] introduced an improvement in the phosphorographic method of investigating the spectrum. By placing sensitive plates of bromide of silver directly on the phosphorescent screen he succeeded in obtaining permanent images. Draper concluded from his experiments that it is an impossibility to secure well-defined maps of the spectrum in this manner, on account of the communication of phosphorescence from particle to particle. Lommel[3] has shown, nevertheless, that fair results may be obtained by this method. He has published some very good maps of the solar spectrum made in this way, and proposes to investigate metallic spectra by the same method. However, he did not succeed in securing any results beyond a wave-length of about 9500 Ångström units. Langley has also made some preliminary experiments in this direction.[4] Unfortunately, only the

[1] *Report of the Secretary of the Smithsonian Institution*, 1894.

[2] *Phil. Mag.* **11**, 160, 1881.

[3] *Wied. Ann.* **40**, 681, 1890.

[4] *Report of the Secretary of the Smithsonian Institution*, 1894.

strongest lines appear on such photographs, and the definition does not seem sufficiently sharp to allow very accurate measurement.

The results attained by the various methods above described have been qualitative rather than quantitative, and no systematic attempt has been made until recently to ascertain to what elements the absorption bands and lines are due, with the exception of the phosphorographic determinations made by H. Becquerel. Recently Snow[1] has investigated the prismatic spectra of the alkali metals with the bolometer for the special purpose of testing the applicability in the infra-red of certain empirical formulæ deduced by Kayser and Runge, which will be referred to later. A flint-glass prism was carefully calibrated by means of interference bands produced in the spectrum by thick glass plates. The positions of the maxima and minima of these bands were determined by a very sensitive bolometer to a wave-length of 26,680 Ångström units. The sensitiveness of the bolometer was estimated to be about $\frac{1}{130000}$ degree for one millimeter deflection on a scale three meters distant. A candle at a distance of one meter caused a deflection of 15^{cm}.

More recently Paschen[2] further improved the bolometer, reaching in some cases a sensitiveness estimated to be one-millionth of a degree for one millimeter deflection on a scale one meter distant from the mirror. Although he used a concave grating for the purpose of calibrating prisms, he seems to have made no determination of special wave-lengths.

There are two possible methods by which wave-lengths in the infra-red may be either directly or indirectly measured. One is the method of interference, of which Snow made use. Michelson[3] has shown that this method is capable of the highest precision, but as ordinarily applied the results are unsatisfactory, owing to the small distances between the maxima and minima and to the difficulty of determining their positions

[1] *Wied. Ann.* **47**, 208, 1892; *Phys. Review*, July and August, September and October, 1893.

[2] *Wied. Ann.* **48**, 273, 1893; **53**, 287, 1894.

[3] *Phil. Mag.* March, 1891, p. 256; *A. and A.* **11**, 884, 1892; *A. and A.* **12**, 556, 1893.

accurately. Snow estimated the probable error of his readings on these bands to be about 5 parts in 1000. Moreover, his bolometer strip covered from 13 to 200 Ångström units, according to its position in the spectrum, and although his observations were made with great care the error in the visible spectrum was on the average about 11, and amounted in some cases to 50 or 60 Ångström units. These errors seem unavoidable in prismatic measurements, especially in the infra-red, owing to the great condensation of that end of the spectrum.

The second and by far the most reliable method of determining wave-lengths is by means of the grating. There are three ways by which this has been done — photographic, phosphorographic and thermometric. The application of the first method to the measurement of infra-red wave-lengths of the elements has proved to be a failure. The second, though greatly improved by Lommel, gives results which are deficient in detail and in definition. At present the last method seems the most satisfactory. The bolometer has given good results in prismatic spectra, but requires great improvement in sensitiveness to give satisfactory results with a diffraction grating, owing to the feeble intensity due to the multiplicity of spectra. For this reason it does not appear that anyone has yet succeeded in detecting the existence of isolated lines in the diffraction spectrum with the bolometer. Professor Langley used a concave grating of about 163^{cm} focal length and 3610 lines per inch for the purpose of calibrating his prism, but the radiation passing through the slit, which was 2^{mm} wide, was by no means homogeneous. In one of these determinations he estimated the probable error to be from 69 to 110 Ångström units, and even with a wide slit the maximum of his galvanometer readings was only about 6^{mm}.[1] Paschen calibrated a prism by a grating similar to that above mentioned, using a very sensitive bolometer, with a strip only $0^{mm}.25$ wide. He estimated the probable error of his individual observations to be from 30 to 100 Ångström units.[2]

[1] *Report of the Mount Whitney Expedition*, p. 220.

[2] *Wied. Ann.* **53**, 287, 1894.

INSTRUMENTS AND METHODS.

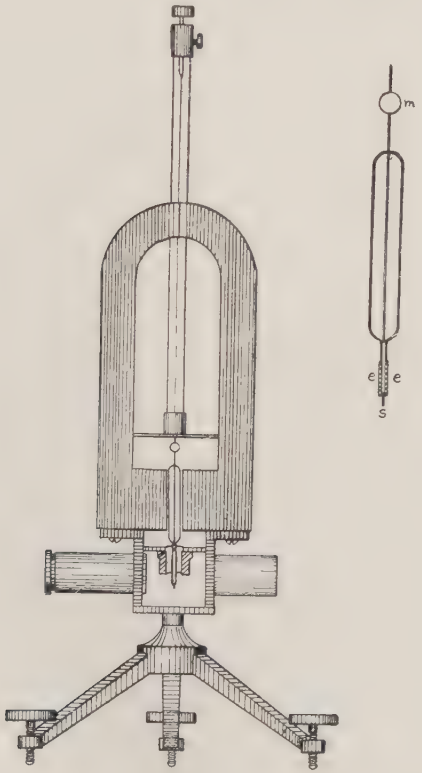
From this review it will be seen that very little has been done towards the identification of lines due to the elements in the infra-red, and practically nothing in the way of their accurate measurement, determinations having been made either by gratings of small dispersion, or by means of calibrated prisms. The latter, at best, is a very imperfect method. It was desirable, therefore, to make some measurements with a grating of high dispersion, provided that means could be devised for detecting the small quantities of heat involved. The present investigation was begun by Mr. E. S. Ferry and the writer, with a bolometer. A detailed description of this instrument and of the efforts made to secure satisfactory results from it has been published.[1] Nothing need be added to the account except the statement that further trial demonstrated conclusively that no reliable results could be obtained from the bolometer under existing conditions.

The radiomicrometer, first used by D'Arsonval and independently invented and greatly improved by Boys, commends itself by its simplicity, its freedom from external disturbances, and its great sensitiveness. It was decided to test this instrument, although it has some serious disadvantages for spectrum work It cannot well be moved through the spectrum, and the strip upon which the radiation falls, being free to vibrate, can neither be located so definitely, nor conveniently made so narrow as the strip of a bolometer. The first difficulty might be overcome by keeping the instrument in a fixed position and moving the slit and the source of light. Since it was intended to use a grating of high dispersion, the other objections were not very serious.

A vertical section of the instrument is shown in Fig. 1. A horseshoe magnet about 25^{cm} high, 4 wide and 2 thick, with a polar gap of 11^{mm}, is screwed vertically to a brass frame supported on a tripod. This magnet was made of chilled cast iron, and has been found to retain its magnetism very well on account of the long magnetic circuit and the short distance between its

[1] *Johns Hopkins Univ. Cir.* 13, No. 112; *A. and A.* November, 1894.

poles. At first the field was too strong, causing excessive damping of the coil, but after being somewhat weakened it proved perfectly satisfactory. By weakening the field, the effects of magnetic impurities in the wire were reduced, as these effects are proportional to the square of the intensity of the field, while the



FIGS. 1 AND 2

deflections due to the current are directly proportional to the magnetic force. The loop of wire and the thermal element were suspended between the poles of the magnet by means of a fiber supported in a long glass tube passing through a hole in the bend of the magnet. The loop was completely enclosed by plates of brass screwed to the poles of the magnet. On one side

was a narrow glass window through which the loop could be observed, and light thrown on the mirror. The thermal element was enclosed by a soft iron tube to screen its diamagnetic material from the magnetic field. The radiation fell on one junction through a tube in front of the instrument, and the element and neighboring portions of the spectrum could be viewed through an eyepiece screwed into the back.

Several months were spent in efforts to make a satisfactory coil and element. The theory of the instrument has been completely worked out by Boys.[1] It was intended to test some of his conclusions by using various sizes of wire and of loop, and different numbers of turns in the coil. However, it was soon found that one difficulty completely overshadowed all the rest; this was to secure wire perfectly free from magnetic impurities. In the preliminary experiments about twenty different specimens of copper were used, and at least seventy-five loops and elements were made and tried, but no comparable results could be obtained. Not only was it impossible to secure great sensitiveness on account of the directive force of the magnetic impurities, but the lack of uniformity of the magnetic field made it difficult to keep the spot of light on the scale. In spite of all efforts to avoid it, the center of the field was less intense than the sides; consequently the tendency of the magnetic coil was to move into the strongest part of the field, so that its plane was at right angles to the lines of force. By fastening such coils in the proper position for several hours they appeared to become permanently magnetized, and when left to themselves would retain that position for some time. There seemed to be a slow viscous change, however, caused no doubt by the shifting of the axes of the magnetized particles, which would in time carry the spot of light off the scale to one side or the other. The magnetic directive force was so great that the fiber had no control whatever over the loop. On one occasion the torsion head was turned through thirty revolutions without perceptibly disturbing the position of the coil. Finally Dr. Ames succeeded

[1] *Phil. Trans.* 1888, p. 159.

in procuring, through the kindness of R. Brent Keyser, Esq., of the Baltimore Copper Company, a piece of very pure copper wire. After being drawn to the proper size (about $0^{mm}.3$ in diameter) its surface was cleaned with chemically pure nitric acid. Coils made of this wire, while not absolutely free from magnetic effects, were found to be easily controlled by a fine silk fiber. The coil used in the final experiments consisted of a single loop of this wire 5^{cm} long and $0^{cm}.6$ wide.

Great difficulties were experienced also in making the thermal elements. Some unsatisfactory tests were made with alloys, but subsequently pure bismuth and antimony were exclusively used. The bars were usually about one centimeter long, and from one-third to one-half millimeter cross section. At first they were made by grinding lumps of the metals down to thin plates and then cutting the bars from these by a fine saw or file. Both metals are difficult to work, and at least nineteen out of twenty of the bars were broken while being made. It was found, however, that these elements could be made very easily by a method due to Noll.[1] The melted metal was sucked up in small thin-walled capillary glass tubes, which were then broken off to the desired lengths. It was difficult to remove the tube from the enclosed metal, so that in most cases it was allowed to remain as an insulation between the two bars, which were bound firmly side by side. Next they were soldered to the ends of the loop of copper wire, and their lower ends joined by a strip of thin copper about one millimeter wide and several millimeters long. A glass fiber was fastened by shellac to the copper loop, and on this was placed a small concave mirror of about one meter focus. The loop was suspended by a fiber, and the deflections were read by means of the image of the filament of an incandescent lamp reflected on a millimeter scale.

The early attempts to obtain measurable deflections in the spectrum of a high-dispersion grating were failures. Success was first attained with Professor Langley's grating, referred to above, which was kindly loaned for the purpose. As adjusted for this

[1] *Wied. Ann.* **53**, 874, 1894.

test, the strip of the radiomicrometer covered about 40 Ångström units in the spectrum. With sodium chloride burning in the arc, and the strip set over the D lines, deflections of about one millimeter were at first obtained. At Professor Rowland's suggestion a cylindrical lens was then placed with its axis parallel to the spectrum so as to shorten the images of the spectral lines and concentrate them entirely upon the strip, which was reduced to about two millimeters in length. By this means deflections of about one centimeter were obtained, but it was impossible to separate the D lines. Since it was very desirable to obtain more accurate results, attempts to use a grating of higher dispersion were resumed. The one finally used was concave, of about fourteen feet focus, and was ruled with 10,000 lines to the inch. The first spectrum was exceptionally bright, and was visible beyond the usual limit at the red end. By substituting a smaller element on the coil previously alluded to the single D lines caused deflections almost as great as those made by both lines in the spectrum formed by Professor Langley's grating. The length of the element was $1^{cm}.3$, the width of the copper strip $0^{cm}.07$, and its length $0^{cm}.2$. This loop was suspended by a silk fiber, no quartz fibers of sufficient fineness being on hand. This coil is represented in Fig. 2; e and e' are the bars, s the strip soldered between their ends, and m the mirror. The various coils made were tested by observing the deflections caused by a candle ten feet distant. With different elements tested the deflections were from one to fifteen centimeters. Comparisons of this kind are, however, no test of the sensitiveness of the element when exposed to a spectral line. As an instance of this, with the coil finally used the deflection caused by the candle was only two centimeters, yet in the spectrum it was far more sensitive than the one mentioned above from which a deflection of fifteen centimeters was obtained. The strip of the latter was twelve square millimeters in area, while that of the former was only 1.4 square millimeters. The cross section of the elements was about the same in the two cases. The size of the strip determines the quantity of heat supplied to the junction,

while the cross-section of the elements determines the amount which flows away, so that the temperature of the junction is evidently a function of the relative area and cross-section. There is no advantage, however, in having the width of the strip greater than that of the spectral lines, and when a cylindrical lens is used to shorten the lines, as in this experiment, it is advantageous to have the area of the surface which receives the radiation of exactly the same size as the image of a line. The possibility of concentrating the radiation in this manner is one great advantage which the radiomicrometer possesses over the bolometer, in using which nothing is gained by making the line shorter than the bolometer strip. The bolometer used in the beginning of this experiment gave a deflection of about three centimeters when exposed to a candle ten feet away, making it apparently more sensitive than the radiomicrometer element which gave only two centimeters deflection, but the area of the bolometer strip was eight times as great. Moreover, the cylindrical lens practically increased the sensitiveness of the radiomicrometer eight or ten times.

In addition to its greater sensitiveness, the radiomicrometer is far more reliable in its indications than the bolometer. When using the latter, nearly all the time of an experiment was spent in adjusting the resistance to balance the drift which constantly manifested itself. The necessary lightness of the galvanometer system also made it impossible to secure steadiness of the spot of light, and thermal effects in the circuit gave trouble. The radiomicrometer is perfectly free from these objections, and if it were possible to move it through the spectrum it would be an ideal instrument.

The arrangement of the spectrometer is shown in Fig. 3. An iron beam, *B*, 15 feet long, is supported on a truck at each end. These trucks roll on two rails, *A* and *C*, placed at right angles. At one end of the beam and adjusted perpendicularly to it is the concave grating *G*. At the other end is the slit *S*, beyond which is attached a box carrying an arc lamp *L*. At the intersection of the rails is the radiomicrometer *R*. The

theory of the concave grating[1] shows that under these conditions the radiomicrometer will always be in focus as the beam carrying the grating and the source of light is displaced, and that the distances through which the slit moves as measured on the rail *A* are proportional to the wave-lengths of the lines which are

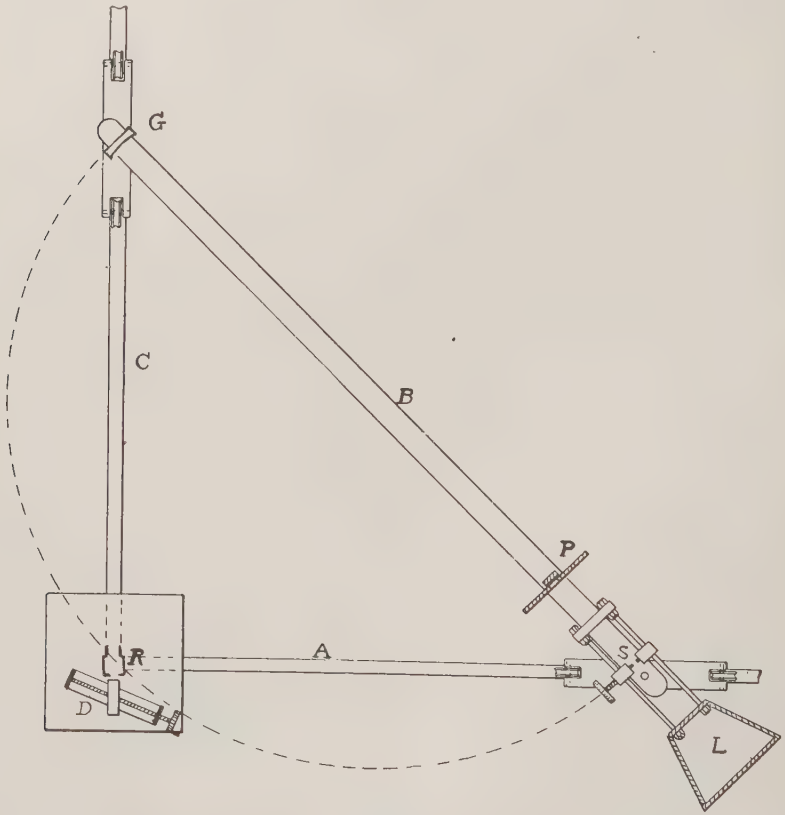


FIG. 3

observed at *R*. The wave-length of any line on which the strip is set may therefore be determined by moving *L* so as to bring known lines successively upon the strip and measuring the distances over which the slit has been moved. Since errors might

[1] ROWLAND, *Am. Jour.* **27**, 1883. Ames, *Phil. Mag.* **27**, 1889. *A. and A.* January, 1892.

arise from flexure of the beam, an attempt was made to use another plan. The eyepiece of the radiomicrometer was removed, and the opening covered with a piece of plane glass. In front of the instrument was placed a dividing engine *D*. On the carriage of the dividing engine was an eyepiece, and it was intended when the strip coincided with an invisible line to set the cross-threads of this eyepiece first on the strip and then on the neighboring known lines of the overlapping second spectrum. The spectra of a concave grating adjusted as in this case lie upon the circumference of a circle (indicated by the dotted line) having the iron beam for a diameter; hence in order to bring lines occupying different positions into the focus of the eyepiece it was necessary to place the dividing engine tangentially to this circle and at an angle with the rail, as shown in the figure. The screw of the dividing engine would, however, be tangent to the circle of spectra only for one position of the beam; consequently it was found impossible in general to bring the lines into focus, and in most of the experiments distances were measured directly on the rail by means of a steel millimeter scale and a vernier reading to tenths. The rail *A* was of such length that the first spectrum could be investigated to about wave-length 16,000.

The arc light was supplied with a current of 22 amperes, under an electromotive force of 110 volts. The carbons used were about one centimeter in diameter. Holes about $1^{mm}.5$ in diameter were drilled in both the positive and negative carbons and filled with a salt of the element under investigation. An image of the arc was thrown by a small glass lens on the slit, which was about $0^{mm}.7$ wide, so that the image of a line would about cover the radiomicrometer strip. The slit itself was mounted on a micrometer screw, so that in cases where the dividing engine was used in measuring distances to known lines the beam could be clamped, the slit moved and the deflections for successive positions plotted. From the curve drawn from these results the position of maximum intensity could be found, the slit set in that position, and distances between the strip and known lines of the second spectrum measured with the dividing

engine. Whenever readings were taken directly on the rail the slit was kept in a fixed position relative to the beam, and the readings were taken by moving the lamp and slit up and down the rail so as to bring known lines of the spectrum upon the radiomicrometer strip. Small quantities of calcium and iron were mixed with the salt to be studied in order to furnish comparison lines.

Unless the grating, the source of light, and the radiomicrometer are exactly on the vertices of a right-angled triangle, the distances on the rail will not be strictly proportional to the wavelengths. No measurable deviation from proportionality could be observed in this case, however, and it was found that comparison lines some distance from the line which was to be measured gave quite as consistent results as those which were nearer.

At P is a screen which prevents the radiation of the arc from falling on the grating. Whenever an observation is to be taken, the slit is set in the desired position and this screen raised. If the strip is set upon a hot line, a deflection will be observed. In about ten seconds this will reach its maximum. On lowering the screen, the coil will slowly return toward its initial position, its motion being perfectly dead-beat. On account of the viscosity of the silk fiber it scarcely ever returns entirely to its zero point; for this reason only the direct deflections are usually observed.

The room in which the observations were taken is on the fourth floor of the physical laboratory. At first great difficulty was experienced from the vibrations of the building, caused by the wind, and by the passing of cable or electric cars, or of loaded wagons over the cobble stones in the street below. This was almost entirely obviated by mounting the radiomicrometer on several slabs of marble and iron laid over each other, with strips of rubber between them. Except when the wind was blowing or heavy vehicles passing, the spot of light was then almost perfectly steady, so that no trouble was found in reading deflections to $0^{mm}.1$.

There are several sources of error which must be taken into account. One millimeter on the rail A corresponds to about

four Ångström units. The strip itself covers a width of three Ångström units in the spectrum. In plotting the curve of intensity of each line there was a probable error in locating the maximum of about $0^{mm}.1$, or 0.4 of an Ångström unit. The setting on a comparison line was also somewhat uncertain, owing to the width of the slit. Errors could also be introduced from flexure of the iron beam, and from mistakes in reading the vernier. A number of settings on known lines showed that the maximum error due to these three causes was $0^{mm}.15$ or 0.6 of a unit. The radiomicrometer strip might also be accidentally displaced during a series of observations. This was guarded against by setting the cross-threads of the dividing engine eyepiece upon it, and examining its position from time to time. All these errors are as likely to occur in one direction as another, and in the course of a long series of observations would largely neutralize each other. An apparent displacement of the maximum of an intensity curve may also arise from irregular burning of the salt in the arc. This was eliminated as far as possible by running the slit first in one direction and then in the other while observing the deflections, so as to average the intensity during a considerable period. One difficulty that seemed to be without remedy was due to the use of the cylindrical lens for focusing the spectral lines on the strip. These lines have two foci — the first, which determines the definition, is that of the grating itself; the second, which determines the maximum shortening of the lines, is that of the lens. In order to secure the greatest heating effect, the strip was placed in the latter focus, by which means the definition of the lines was so impaired as to make accurate settings on comparison lines difficult.

Although the region investigated was under the second spectrum, the latter was very feeble, and no trouble was experienced on this account. At points where deflections were observed, eye observations would at once determine whether they were due to visible or invisible lines. By making observations with and without the salt under investigation in the arc, it could also be determined whether any line found in the infra-red was due to that substance.

RESULTS.

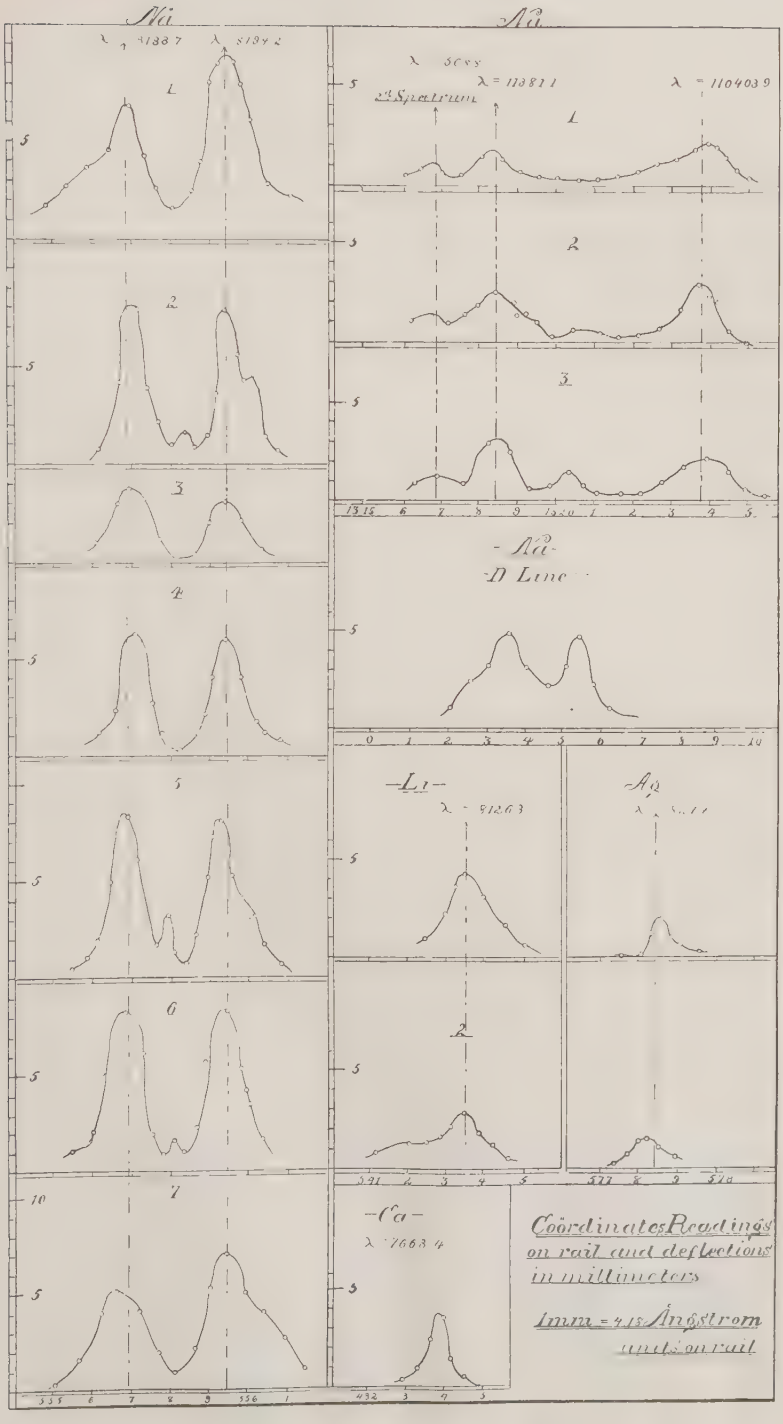
SODIUM.

Before undertaking any systematic investigation of the infra-red spectrum of any one element, it was deemed advisable to endeavor to make accurate measurements of some of the more intense lines whose positions had been approximately determined by Becquerel and by Snow. A search was first made for the sodium lines which these observers found at wave-lengths 8190 and 8180 respectively, and which had been shown by Abney to be double. The pair was soon found, and a number of observations made upon them. In order to guard against error, their curves were mapped repeatedly. The results are shown below. In order that these observations might be as absolutely unprejudiced as possible, the position of the radiomicrometer was slightly shifted before each series of observations, but in the curves here given the readings are all reduced to the same origin in order that comparisons may be more easily made. As an indication of the great labor and the time required in making these measurements it may be mentioned that the curves for this one pair of lines represent the observation of over 800 deflections, not counting those which were observed in looking for the lines.

Below is a typical set of readings, the results of which are shown in curve No. 1, Plate II. Four deflections were observed in each position of the slit, two being taken while moving the slit up the rail, the others when moving it back. The deflections are in millimeters, and the numbers at the head of each column represent the readings on the rail, in centimeters:

55.5	55.55	55.6	55.65	55.675	55.7	55.725	55.75	55.8
2	3	4	5.3	7	5	5.6	1.8	3
1.5	2.5	3.6	5	5	6.8	3	2.2	0
1.7	2	4.5	5	5.5	8.4	4.8	3.5	2
2	4	3.6	7.1	5.4	7.2	4	2.6	0.5
1.8	2.9	3.9	5.6	5.7	6.8	4.3	2.5	1.4

PLATE II


Ni
Na
Coördinates Readings on rail and deflections in millimeters
1mm = 4.15 Ångstrom units on rail

55.85	55.875	55.9	55.925	55.95	55.975	56.0	56.05	56.1
2	3.5	8.1	8.8	9	8.4	6.2	3.2	1.8
2.8	3.5	10	9	10.5	6.8	6.3	1.8	2
2.5	4.4	7.2	8.5	7.8	8	6.8	3.1	3
3.5	5.0	7.5	10	10	8.6	6	3.8	2.6
2.7	4.1	8.2	9.1	9.3	8	6.3	3	2.6

The agreement between these curves is in general very good. There are differences in their height due to varying quantities of salt in the arc, but the positions of their maxima correspond as well as could be expected. In three of these curves (Nos. 2, 5 and 6) there are indications of a feeble line between the pair due to some impurity. A slight irregularity on the right side of one of the lines seen in curves Nos. 2, 5, 7, may be due to an iron line in the second spectrum of wave-length 4098.3, since a small quantity of iron was used in the arc to produce comparison lines. No evidence of reversal is perceptible. In fact, on account of the width of the strip, the only result of reversal would be a slight flattening of the curves. The deflections obtained from the D lines were about the same as those for this pair, indicating that they are of about equal intensity.

On one or two occasions, when a large amount of salt was in the arc, this pair of sodium lines was barely visible. They were so hazy and diffuse, however, that no eye measurements could be taken.

Below are the wave-lengths of the sodium pair as determined from the various curves. In cases where readings were taken on the rail, the wave-lengths were calculated for the first line, and to the average of these results (each of which was determined from one comparison line) was added the number of units corresponding to the distance between the maxima on the curve in order to obtain the second line. In the set of readings obtained from the dividing engine independent determinations were made

for each line. In the second set of observations only two readings on comparison lines were obtained, owing to an accidental displacement of the dividing engine. (Columns marked D were measured by the dividing engine; those marked R direct on the rail).

1 (R)	2 (D)	3 (R)	4 (D)	5 (R)	6 (R)	7 (R)
8184.19	8184.14	8183.54	8184.50	8183.76	8183.71	8182.67
8184.31	8184.52	8183.66	8183.89	8183.27	8183.58	8182.57
8182.96		8184.16	8184.44	8183.17	8184.27	8182.55
8184.70		8184.24	8184.41	8183.64	8183.26	8182.56
8182.53		8183.83	8183.69	8183.75	8182.53	8183.36
8184.11					8183.94	
8183.52						
8183.73	8184.33	8183.84	8184.19	8183.52	8183.55	8182.74

General average, 8183.73.

			8194.15			
			8194.08			
			8194.43			
			8194.09			
			8193.17			
10.63		10.87		10.44	10.44	11.69
8194.36		8194.71	8193.98	8193.96	8193.99	8194.43

General average, 8194.24.

The close agreement between these results indicates that the error of the mean can hardly be as great as one Ångström unit, and probably does not exceed 0.5.

It should be noted that Abney did not claim any great accuracy in his measurement of this pair. The nearest lines to the above given in his table for the solar spectrum are 8184.4 and 8193.4, to which must be added about 1.4 to reduce from Ångström's to Rowland's scale, giving 8182.8 and 8194.8.

Balmer showed that the wave-lengths of certain series of lines in the hydrogen spectrum could be represented with surprising accuracy by the empirical formula $\lambda = h\frac{n^2}{n^2-4}$, n representing the successive ordinal numbers above 2 and h a constant.[1] Later Kayser and Runge showed that in the spectra of nearly all the elements there are series of lines whose positions can be expressed by empirical formulæ of the form

$$\frac{1}{\lambda} = A + Bn^{-2} + Cn^{-4} + \ldots\ldots$$

where $\frac{1}{\lambda}$ is a number proportional to the frequency and n represents the successive ordinal numbers.[2] They have also found that in cases where series of pairs occur, as in the case of sodium, the difference of the values of $\frac{1}{\lambda}$ between the two members of any pair is a constant for that element. The average value of this difference for sodium is 172. The difference shown by the above results is 160, which is as close agreement as is found with some pairs in the visible spectrum. Kayser and Runge have predicted from their empirical formulæ the occurrence of various lines in the infra-red. They appear to have used Abney's values for the pair discovered above, reduced to Rowland's scale, for the determination of the constants of their formulæ for sodium, and have predicted the existence of another pair of wave-lengths 11481.8 and 11504.8, which perhaps correspond to a line discovered by Becquerel of wave-length 11420 and given by Snow as 11320. The neighborhood of the spectrum corresponding to these lines was explored several times without success. At last, by using large quantities of sodium chloride in the arc, they were discovered just above the sodium pair 5682 and 5688, in the second spectrum. The readings made on them were as follows:

[1] *Wied. Ann.* **25**, 80, 1885.

[2] *Abhand. d. K. Akad. d. W. Berlin*, 1888–93.

	I	II	III
	11378.26	11381.35	11381.76
	11381.72	11381.59	11382.00
	11382.43	11381.05	11381.46
	11381.50	11379.84	11380.68
	11380.50	11380.93	11381.77
	11380.88	11380.95	11381.53
Add distance, between maxima	23.20	22.57	22.60
	11404.08	11403.52	11404.13

General averages { 11381.12 / 11403.91

The agreement of these observations is not so good as of those lower in the spectrum on account of difficulty in focusing on comparison lines. The intensity of these lines seems about one-third that of the other infra-red pair. Their difference in frequency is 176.

No absorbents were used to cut out the second spectrum in these observations. As is well known, sodium or potassium in the arc will almost eliminate the carbon spectrum, and visible lines were easily avoided. That the lines were actually due to sodium was demonstrated by the fact that no deflections were obtained unless sodium was in the arc.

The results for sodium are compared with those of other observers below:

Becquerel	Snow	Abney	Kayser and Runge (calc.)	Lewis
8190	8180	8187	——	8183.7
—	—	8199	——	8194.2
11420	11320	—	11481.8	11381.1
—	—	—	11504.8	11403.9

LITHIUM.

Snow found a lithium line of wave-length 8110, while Kayser and Runge predicted its occurrence at about 8190. They considered, however, that under the circumstances this was a sufficiently close agreement with Snow's result. I have found

this line and made the following measurements of its wave-length:

I	II
8127.03	8125.91
8125.86	8126.03
8126.99	8126.99
8125.97	8126.43
8126.47	8125.52
8126.08	.....
8126.40	8126.16

General average, 8126.3

Becquerel gives no results for lithium.

SILVER.

Becquerel gives the wave-lengths of two silver lines as 7710 and 8250, and describes them as being very intense. Kayser and Runge predict the existence of silver lines of wave-lengths 7695 and 8282. A line apparently corresponding to the last was found without difficulty. Below are the measurements:

I	II
8274.49	8273.29
8274.52	8272.99
8274.00	8274.13
8274.47	8273.97
8275.29	8273.32
8274.55	8273.54

General average, 8274.04

While searching for the other line, rather feeble indications of its existence were given by the radiomicrometer. The line was found to be faintly visible, and its wave-length was determined by eye observations as follows:

7687.79
7687.91
7688.44
7689.14
7688.65
7688.4

CALCIUM.

A systematic search for calcium lines in the infra-red was begun, but so far it has been unsuccessful except in the case of a line which is faintly visible. The result is an evidence of the reliability of the radiomicrometer. By means of it alone the line was found and its wave-length determined as follows:

7663.38
7663.30
7664.06
7662.60
7663.81
7663.43

It was subsequently found to be visible under favorable conditions, and from eye observations its wave-length was determined to be 7663.76. This is almost coincident with a strong potassium line, but since the deflections caused by it were greater than those obtained when potassium was burning in the arc, it is probably really due to calcium, and not to traces of potassium.

Becquerel observed indications of groups of calcium lines between 8580 and 8880. A preliminary survey has been made of this region, without discovering any intense lines. The curves for lithium, silver and calcium lines show no marked peculiarities. The investigation will be continued and it is hoped that other lines may shortly be discovered.

An effort was made to determine the position of several potassium lines discovered by Becquerel and Snow, but on account of their feeble intensity they could not be detected with certainty.

Several improvements in the radiomicrometer have suggested themselves during these experiments, but have not been adopted on account of lack of time. The copper wire used for the loop should be drawn through jeweled plates in order to avoid all contact with iron. By using copper which is absolutely pure, and suspending the coil by a very fine quartz fiber, there seems to be hardly any definite limit to the possible sensitiveness of this instrument. The coil should also be lighter, in order that it

may respond more quickly to heating effects, and the width of the strip should be less in order to have greater resolving power in the spectrum. In order to prevent losses by absorption, which would be very serious further in the infra-red, lenses should be dispensed with and the image of the arc thrown upon the slit by a concave mirror. The radiation should be focused upon the strip by means of a cylindrical parabolic mirror, cut away near the vertex to allow the strip to be placed at the focus. The arc and slit should also be mounted on a carriage moved by a micrometer screw, so that more accurate measurements can be taken.

My thanks are due to Professor Rowland and to Dr. Ames for their suggestions and for their continued encouragement at times when success seemed almost hopeless.

JOHNS HOPKINS UNIVERSITY,
May, 1895.

BIOGRAPHICAL SKETCH

The writer of this thesis, Exum Percival Lewis, was born September 15, 1863, in Tyrrel County, North Carolina. He studied the elementary English branches at home. In 1884 he entered the Corcoran Scientific School, Columbian University, from which he graduated in 1888 with the degree of B. S.

In 1890 he entered the Johns Hopkins University as an honorary Hopkins Scholar from North Carolina. The following year he was appointed assistant in physics, a position which he still holds.

His principal subject of study has been physics; his subordinate subjects, mathematics and astronomy.